Substituent effects in the ^{13}C nuclear magnetic resonance spectra of aryl ether copolymers: 4. Materials containing sulphonated aryl rings

Raymond J. Abraham* and Ian S. Haworth
The School of Chemistry, The University of Liverpool, PO Box 147, Liverpool, L69 3BX, UK

Alan Bunn and R. Angus Hearmon
ICI Wilton Materials Centre, PO Box 90, Wilton, Middlesbrough, TS6 8JE, UK
(*Received 22 March 1989; accepted 27 April 1989*)

Polymeric materials containing 1,4-disubstituted aryl rings with ether (E), ketone (K) and/or sulphone (S) linkages, and in which certain rings are monosulphonated, give extremely complex ^{13}C nuclear magnetic resonance (n.m.r.) spectra. The quaternary carbon atom shifts, which are particularly sensitive to changes in the monomer sequences and sulphonation pattern, have been assigned to specific sequences and pattern differences, with signals characterized by either *ortho* or *meta* sulphonation of rings up to three rings distant from the observed carbon atom (C*) being resolved. The shifts obtained for the sulphonated ES/EES copolymer, when compared with those of the non-sulphonated material, suggest the major transmission mechanism for sulphonation effects to be via the π system, with a possible anisotropic effect contributing to the longer-range shifts, induced by the specific conformation the chain adopts. This argument leads to a full assignment, including specific sulphonation patterns, of the sulphonated ES/EES copolymer ^{13}C n.m.r. spectrum in deuterated dimethylsulphoxide (DMSO-d_6).

(Keywords: aryl ether; aryl sulphone; aryl ketone; copolymer; sulphonation; ^{13}C nuclear magnetic resonance; substituent effect)

INTRODUCTION

Sulphonation of polymeric aryl ether-containing materials and, in some cases, further modification of the sulphonate, has been extensively used to improve the hydrophilicity[1] and, due to a reduction in crystallinity, the solubility[2] of the polymers whilst retaining their excellent mechanical and thermal properties[3–5]. As for any electrophilic substitution, the severity of the required conditions is dependent on the degree to which the ring is activated or deactivated towards the incoming electrophile, and several procedures have been described for the sulphonation of polymeric aryl ether materials. The di-ether flanked ring in poly(aryl ether ether ketone) (PEEK) is monosulphonated[2,6], without appreciable degradation, by dissolution in concentrated sulphuric acid (a small amount of water must be present to prevent crosslinking via sulphone formation[6]). Conversely the ^1H n.m.r. spectrum of poly(aryl ether ketone) (PEK), which only contains rings substituted by one ether and one carbonyl function, shows no evidence of sulphonation having occurred in sulphuric acid[7]. Generally less activated rings require, in addition to higher temperatures and longer reaction times, reagents such as chlorosulphonic acid[8,9] or SO_3 with triethyl phosphate[9,10], and dissolution of PEEK in the former does cause some sulphonation of the oxycarbonyl rings, probably *ortho* to the ether function[6].

Spectral characterization of the sulphonated materials has depended on infra-red[1,2,6,8] and, to an extent, ^1H n.m.r. spectroscopy, the latter technique being particularly applicable to the determination of the degree of sulphonation[1,11]. ^{13}C n.m.r. spectra of these materials have not been extensively reported; however, confirmation of the maximum attainable level of PEEK sulphonation in sulphuric acid was obtained from the deuterated dimethylsulphoxide (DMSO-d_6) solution spectrum of the recovered material[2]. It was further observed that each of the quaternary carbons of the oxycarbonyl rings neighbouring the sulphonated di-oxy ring were split into two signals, suggesting a long-range effect of the sulphonic acid function, either through space or bonds, on the carbon chemical shifts. The sensitivity of the quaternary carbon shifts in non-sulphonated aryl ether-containing materials has been shown in previous parts of this series[12–14] and it seems probable that similar effects should be present for the sulphonated polymers.

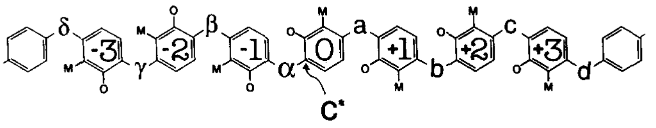
Qualitative[12] and quantitative[13,14] interpretations of the complex signal patterns observed for the quaternary carbon signals in the DMSO-d_6 solution spectra of copolymers containing 1,4-disubstituted rings and various bridging groups have led to the derivation of a series of shift parameters for the sulphone and ketone[13], biphenyl[14] and sulphide[15] functionalities. These parameters are based on a poly(aryl ether) chain having a quaternary carbon atom C* (see below), and describe the change in chemical shift of C* caused by replacing an ether function by an alternative bridging group at each position (i.e. α, β, a, b, etc.). In extending this approach to include sulphonation effects, additional nomenclature is introduced. Thus, for example, the four sulphonating positions in the di-oxy ring in PEEK are clearly chemically equivalent; however, with respect to the chemical shift of a specific quaternary carbon atom there are two

---

* To whom correspondence should be addressed

0032-3861/90/010126–04$03.00

inequivalent sulphonation sites. Relating this to the poly(aryl ether) base chain, these sites are designated *ortho* and *meta*, depending on their orientation with respect to C*. Numbering of the rings (see below) then allows a complete description of the sulphonation pattern and monomer (bridging group) sequence which give rise to a specific signal in the ^{13}C spectrum.



EXPERIMENTAL

Sulphonated copolymers were prepared by dissolution of the copolymer in concentrated sulphuric acid, using long reaction times to ensure that the maximum level of sulphonation was attained. The material was then recovered by precipitation with water.

Spectra were recorded on a Jeol FX270 spectrometer at 80°C in DMSO-d_6 solution, using conditions similar to those previously described[12]. Chemical shifts were referenced to the central peak of the DMSO-d_6 multiplet (39.6 ppm).

DISCUSSION

Sulphonated aryl ether sulphone/aryl ether ether sulphone copolymer (sES/EES)

The arguments outlined above for PEEK are also applicable to PEES and the random ES/EES copolymer, i.e. only sulphonation of the di-ether flanked rings occurs in concentrated sulphuric acid due to the deactivation of other rings by the sulphone function. The DMSO-d_6 solution spectrum of the recovered material (*Figure 1*) is complex and signals for the quaternary carbons (1–20) can only be assigned by considering changes in sulphonation pattern and functional groups at considerable distances from C*. We have already shown[13] that quaternary carbon signals resulting from sequences differing in the 'δ' and 'd' positions (i.e. ether or sulphone functionality) can be resolved in the DMSO-d_6 solution spectrum of non-sulphonated ES/EES, so the invocation of long-range sulphonation effects seems entirely reasonable. An assignment of the sES/EES quaternary carbon signals is given in *Table 1* and, as for the non-sulphonated material, three distinct signal groups are seen, which are characterized by different 'α, a'-diad functionality[13].

Table 1 Assignments for the sulphonated ES/EES copolymer

Signal number	Sequence								Shift (ppm)	ES/EES^a shift (ppm)
	δ^{-3}	γ^{-2}	β^{-1}	α^0	a^1	b^2	c^3	d		
1	E	S	E^o	E	S	E	S	E	162.44	161.18
2	E	S	E^o	E	S	E^m	E	S	162.36	161.06
3	E	S	E^o	E	S	E^o	E	S	162.20	161.06
4	E	S	E^m	E	S	E	S	E	161.16	161.18
5	E	S	E^m	E	S	E^m	E	S	161.08	161.06
6	E	S	E^m	E	S	E^o	E	S	160.92	161.06
7	Y^y	E	S	E	S	E	S	E	159.10	159.11
8	Y^y	E	S	E	S	E^m	E	S	159.01	158.98
9	Y^y	E	S	E	S	E^o	E	S	158.85	158.98
10	Y^y	E	S	E^m	E	S	E^y	Y	150.41	151.20
11	Y^y	E	S	E^o	E	S	E^y	Y	147.28	151.20
12	S	E^o	E	S	E	S	E^y	Y	137.13	136.88
13	S	E^m	E	S	E	S	E^y	Y	136.81	136.88
14	E	S	E	S	E	S	E^y	Y	136.55	136.55
15	S	E^o	E	S	E^m	E	S	E	135.64	135.32
16	S	E^m	E	S	E^m	E	S	E	135.32	135.32
17	E	S	E	S	E^m	E	S	E	135.06	135.00
18	S	E^o	E	S	E^o	E	S	E	134.34	135.32
19	S	E^m	E	S	E^o	E	S	E	134.02	135.32
20	E	S	E	S	E^o	E	S	E	133.76	135.00

^{a} Non-sulphonated ES/EES shifts from ref. 13

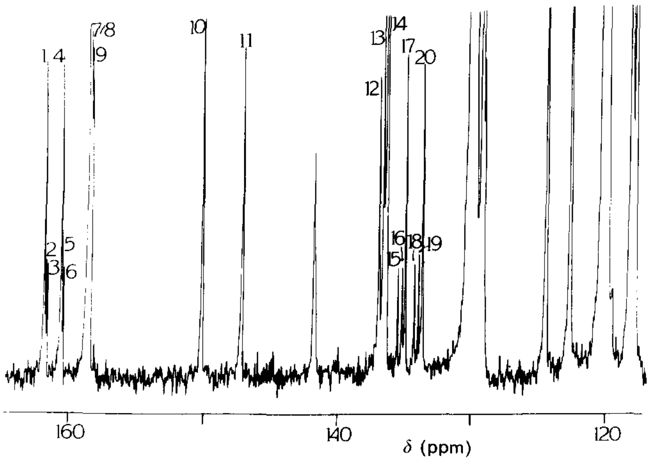


Figure 1 The ^{13}C n.m.r. spectrum of sulphonated ES/EES copolymer

For sequences having an EE 'α, a'-diad (10 and 11) the shift is dependent only on the sulphonation pattern in ring 0. A qualitative comparison of the calculated shifts (obtained from the ES/EES shift[13] and aryl ring substituent effects, +0.8 (*meta*) and −2.7 (*ortho*), for the sulphonic acid group[16]) shows signal 10 to arise from the sequence having *meta* sulphonation in ring 0 with signal 11 due to *ortho* substitution. Quantitatively, however, the sulphonic acid group produces a much larger upfield shift (from the ES/EES value of 151.19 ppm) of the *ortho* quaternary carbon, compared to the literature substituent shift of −2.7 ppm[16], whilst the *meta* quaternary carbon shift is also upfield of the non-sulphonated signal, in contrast to the downfield shifts observed for *m*-SO_3X groups in monosubstituted rings[16]. The occurrence of the non-sulphonated EE 'α, a'-diad signal downfield of the sulphonated signals also occurs in the sPEEK (partially sulphonated) DMSO-d_6 spectrum[2].

One further point regarding signals 10 and 11 concerns possible functionality variation in the 'δ' and 'd' positions, and, for sequences having an ether function in either or both of these positions, possible sulphonation effects from ring −3 and/or ring +3. Both 10 and 11 might, on this basis, conceivably consist of nine signals: four from functionality differences, of which one—that having both 'δ' and 'd' ether functions—is further split into four signals having differing sulphonation patterns in +3 and −3; a further two—those having either a 'δ' or a 'd' ether—are split into two signals reflecting sulphonation effects from rings −3 and +3 respectively; and the remaining sequence having sulphone functionality at both 'δ' and 'd' positions and hence no superimposed sulphonation effects. Signals 10 and 11 are broad, which might indicate fine structure, and a higher-field spectrometer may allow some or all of the nine signals to be resolved. In *Table 1* 'Y' indicates unresolved sequencing information and 'y' unresolved sulphonation pattern information.

The ES 'α, a'-diad signals consist of three groups, each containing three signals. The high-intensity signal 7 is readily assigned to the PES homopolymer sequence (the ES/EES material was predominantly ES in nature), which, since it contains no rings that can be sulphonated by concentrated sulphuric acid, occurs at a similar shift to the sequence in non-sulphonated ES/EES (again the resolution is too low to observe sequencing information in the δ position). The accompanying signals (8, obscured by the PES signal, and 9) arise from the SESEE (β, α, a, b, c) sequence and are characterized by different sulphonation patterns in ring +2. A similar splitting is observed for signals 2, 3 and 5, 6, whilst the signal groups 1–3 and 4–6 differ in the sulphonation pattern of ring −1; however, in both cases there are insufficient data to allow a direct assignment of each signal to either *meta* or *ortho* sulphonation. The specific sulphonation patterns given (*Table 1*) will be justified, on the basis of larger effects induced by *ortho* substitution, in a later section. Much the same arguments may be applied to the SE 'α, a'-diad sequences, giving the assignments for signals 12–20, and, in each case (ES and SE signals), the signal intensities are consistent with a predominantly ES-containing ES/EES copolymer, the effect of sulphonation being to reduce further the intensity of sequences containing one or two EE units, since these are split into two and four distinct signals respectively.

Sulphonated poly(aryl ether ether ketone) (sPEEK)

Partially resolved ^{13}C spectra of partially and fully sulphonated PEEK have been recorded and assigned by Jin *et al.*[2] and our more detailed assignments are based on these spectra. Four distinct signals were resolved for each of the quaternary carbon atoms in the oxycarbonyl ring, reflecting, for the EK 'α, a'-diad sequences, sulphonation patterns in rings −1 and +2 and, for the KE 'α, a'-diad sequences, similar information from rings +1 and −2. Once again it is not possible to define the specific pattern in each ring from a direct observation of the spectrum; however, the same rationale (see next section) employed for sES/EES can be used to obtain the sulphonation patterns given in *Table 2*. There is a constant difference of about 0.2 ppm between the absolute shifts given by Jin *et al.*[2] and those in *Table 2*, since different reference signals were used.

Table 2 Assignments for sulphonated PEEK

Signal number	Sequence δ^{-3}	γ^{-2}	β^{-1}	α^{0}	a^{1}	b^{2}	c^{3}	d	Shift (ppm)	PEEK shift[a] (ppm)
1	E	K	E^o	E	K	E^m	E	K	161.77	160.53
2	E	K	E^o	E	K	E^o	E	K	161.59	
3	E	K	E^m	E	K	E^m	E	K	160.50	
4	E	K	E^m	E	K	E^o	E	K	160.32	
5	E^y	E	K	E^m	E	K	E^y	E	150.71[b]	151.52
6	E^y	E	K	E^o	E	K	E^y	E	148.02[b]	
7	K	E^o	E	K	E^m	E	K	E	132.23	131.90
8	K	E^m	E	K	E^m	E	K	E	132.12	
9	K	E^o	E	K	E^o	E	K	E	131.95	
10	K	E^m	E	K	E^o	E	K	E	131.84	

[a] Shifts for non-sulphonated PEEK, see ref. 13

[b] Literature values[2] of 151.02 and 148.17 ppm

Sulphonation effects

A parameter describing the shift difference caused by *ortho* vs. *meta* sulphonation can be evaluated for each ring directly from *Tables 1* and *2*. These values are designated X_J (where J is 0, −1, +1, etc.) and are given in *Table 3*. A comparison of X_J parameters for sPEES with those for sPEEK shows a number of trends. First, the X_{-1} and X_{+2} values are similar for each case, whilst the X_{+1} and X_{-2} values for PEES are larger than those for PEEK. For the former case the values are derived from, in each case, sequences having C* bonded to oxygen (with a *para* sulphone or ketone function), i.e. a 'similar' carbon atom in each material, whilst the latter values originate from sequences having C* bonded directly to the ketone or sulphone functionality, where the nature of the carbon atom is relatively dissimilar in the two materials. The different values of S_{0o} (the absolute shift of C* induced by *ortho* sulphonation in ring 0) might be explained by slightly different bonding geometries of the sulphonic acid function induced by the different ring conformations in the two polymers, since the preferred conformations of the relevant monomers, benzophenone[17] and diphenylsulphone[18], are significantly different in solution. Conformational changes may also be necessary to accommodate the cations in the sulphonate salts.

As explained earlier, it is not possible to deduce the exact sulphonation patterns, other than for ring 0. However, values can be obtained from the sES/EES spectrum which give the absolute shift caused by *ortho* and *meta* substitution in each ring (S_{J_o} and S_{J_m} respectively, where J is the ring number), and these are listed in *Table 4*. Again it should be emphasized that for all rings other than ring 0 it is unclear which is the *ortho* shift and which is the *meta*. For the +1 and −1 rings,

Table 4 S_{Jj} values for the ES/EES system in DMSO-d$_6$

Ring J	S_{Jj} (j is o or m)	
0	−3.92[a]	−0.79[b]
+1	−1.24	0.06
−1	1.28	0.00
+2	−0.24	−0.08
−2	0.58	0.26

[a] S_{0o}, [b] S_{0m}

Table 3 Sulphonation parameters (X_J and S_{0j}) in DMSO-d$_6$

Polymer	C–S[a]	S_{0o}	S_{0m}	X_0	X_{+1}	X_{-1}	X_{+2}	X_{-2}
PEES-SO_3H[b]	141.82	−3.92	−0.79	3.13	1.30	1.28	0.16	0.32
PEEK-SO_3H	141.59	−3.50	−0.81	2.69	0.28	1.27	0.18	0.11
PEES-SO_3Na	141.76	−3.51	−0.66	2.85	1.21	1.17	0.13	0.35
PEEK-SO_3Ca	141.56	−3.39	−0.71	2.68	–[c]	1.31	0.14	0.23

[a] Shift of the carbon atom directly bonded to the sulphonate group

[b] Obtained from the sES/EES spectrum

[c] Either 1.01 or 0.78, unable to say which since one of the quaternary signals is obscured

however, it is reasonable to assume that the large absolute effects are due to *ortho* sulphonic acid groups, with the effect being predominantly transmitted through the π system via the functional group bridges, which have been shown to transmit effects over several rings in a number of studies[19–21]. In a SE 'α, a'-diad sequence sulphonation of ring +1 in the *ortho* position would clearly affect the π density at the ring +1 quaternary carbon closest to C*, and, via the bridging 'a' ether group, the electron density in ring 0 and at C*, to a greater extent than sulphonation in the *meta* position (from simple resonance structures). A similar argument can be applied to sulphonation of ring −1 in an ES 'α, a'-diad sequence, explaining why there is essentially no effect produced by *meta* sulphonation of rings +1 and −1. Analogously the larger absolute shift observed for rings +2 and −2 can be reasonably attributed to *ortho* substitution with a similar mechanism for transmission, since C* is shifted in the same direction, but to a lesser extent, as that caused by *ortho* substitution of the corresponding inner ring (hence both +1 and +2 *ortho* substitution shifts C* to high field). If the *meta* sulphonation effects from +2 and −2 were purely resonance effects, it seems reasonable to assume they should both be zero. Since this is not the observed behaviour, a possible explanation is to invoke an anisotropic contribution caused by the specific conformation the chain adopts, pushing the outer sulphonic acid groups closer to C* than they appear to be in the extended chain. This may be particularly true of ring +2, in which both *ortho* and *meta* effects are larger than expected from a pure resonance effect, it is possible that the additional 'through-bond' chain length between C* and ring +2, compared to ring −2, allows ring +2 to be closer to C*. These arguments allow a full assignment, including precise sulphonation patterns (*Table 1*), of the sulphonated ES/EES copolymer in DMSO-d_6, using the parameters given in *Table 4*, where those in the left column are now specifically designated as *ortho* sulphonation effects. Application of the same ideas also allows full assignment of the sPEEK spectrum (*Table 2*) and it is hoped to confirm these assignments experimentally in a later communication, using model compounds and low-molecular-weight materials.

ACKNOWLEDGEMENTS

We thank the SERC and ICI (Advanced Materials Group) for a CASE studentship (to I.S.H.).

REFERENCES

1 Johnson, B. C., Ylgor, I., Iqbal, M., Wrightman, J. P., Lloyd, D. R. and McGrath, J. E. *J. Polym. Sci., Polym. Chem. Edn.* 1984, **22**, 721

2 Jin, X., Bishop, M. T., Ellis, T. S. and Karasz, F. E. *Br. Polym. J.* 1985, **17**, 4

3 Stening, T. C., Smith, C. P. and Kimber, P. J. *Mod. Plast. Int.* 1982, March, 54

4 Bailly, C., Williams, D. J., Karasz, F. E. and MacKnight, W. J. *Polymer* 1987, **28**, 1009

5 Attwood, T. E., Dawson, P. C., Freeman, J. L., Hoy, R. J., Rose, J. B. and Staniland, P. J. *Polymer* 1981, **22**, 1096

6 Bishop, M. T., Karasz, F. E., Russo, P. S. and Langley, K. H. *Macromolecules* 1985, **18**, 86

7 Iwakura, Y., Uno, K. and Takiguchi, T. *J. Polym. Sci. (A-1)* 1968, **6**, 3345

8 Lee, J. and Marvel, C. S. *J. Polym. Sci., Polym. Chem. Edn.* 1984, **22**, 295

9 Litter, M. I. and Marvel, C. S. *J. Polym. Sci., Polym. Chem. Edn.* 1985, **23**, 2205

10 Ogawa, T. and Marvel, C. S. *J. Polym. Sci., Polym. Chem. Edn.* 1985, **23**, 1231

11 Noshay, A. and Robeson, L. M. *J. Appl. Polym. Sci.* 1976, **20**, 1885

12 Bunn, A. *Br. Polym. J.* 1988, **4**, 307

13 Abraham, R. J., Haworth, I. S., Bunn, A. and Hearmon, R. A. *Polymer* 1988, **29**, 1110

14 Abraham, R. J., Bunn, A., Haworth, I. S. and Hearmon, R. A. *Polymer* 1989, **30**, 1969

15 Abraham, R. J., Haworth, I. S., Bunn, A. and Hearmon, R. A. unpublished results

16 Ewing, D. F. *Org. Magn. Reson.* 1979, **12**, 499

17 Abraham, R. J. and Haworth, I. S. *J. Chem. Soc., Perkin Trans. 2* 1988, 1429

18 Abraham, R. J. and Haworth, I. S. *Magn. Reson. Chem.* 1988, **26**, 252

19 Attwood, T. E., Newton, A. B. and Rose, J. B. *Br. Polym. J.* 1972, **4**, 391

20 Ueda, M. and Sato, M. *Macromolecules* 1987, **20**, 2675

21 Colquhoun, H. M. and Lewis, D. F. *Polymer* 1988, **29**, 1902